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Theory of the driving force for electromigration*

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Using a linear-response formalism coupled with an infinite resummation, expressions are derived for the driving force of electromigration for a system of independent electrons moving among an array of self-consistently screened ion potentials. We assume that the net scattering is weak, but do not expand in powers of the individual-ion scattering strengths nor do we take an average over the configuration of neighbors about the electromigrating ion. Our final formulas, which are tractable for evaluation, may be understood in terms of solutions of the Boltzmann equation. We discuss this interpretation and show how it resolves the question of the existence and quantitative significance of the Landauer resistivity dipoles. We also comment on the still-unresolved question of the "direct" force.

I. INTRODUCTION

When large steady electronic-current densities are passed through metals the atoms are also observed to undergo directed flow. This phenomenon of electromigration has been extensively studied,[1,2] especially so recently owing to its technological importance in thin-film circuitry.[3] On the theoretical side there has been a resurgence of interest in the past few years owing to the realization that important questions of principle remained to be answered.[4-9]

These questions center on what driving force acts to cause the electromigration. To consider this problem, first note that the Born-Oppenheimer approximation allows one to calculate the driving force by taking the ion in question to be stationary. This approximation finds its validity in the small electron-mass to atomic-mass ratio and in the high temperature necessary for observable atomic motion. One may then conceptually divide the driving force into two pieces: First, what we call the direct force, the applied electric field acting on the bare nuclear charge; and second, what we call the indirect force, the consequence of the applied electric field acting on the electrons causing them to polarize and/or conduct, thereby changing their spatial distribution and yielding an induced force on the nucleus in question. Thus one must not only consider the electric field acting directly on the nucleus but also must take into account the response of the electrons to the field and the new force they subsequently exert on the nucleus. This response may be viewed easily in two extremes. First for tightly bound core electrons one expects the response to be solely polarization. Such electrons do not conduct. In fact when one works through the algebra,[10] the response of such core electrons merely acts to effectively reduce the bare nuclear charge to the valence charge of the ion in question. The other extreme of electronic response is conduction. This gives rise to a force on an ion due to the momentum exchange between the drifting electrons and the ion in question. Such a source of induced force has the pictorial name of "electron wind." The theoretical problem arises in the attempt to treat these two extremes of electron response (and the possible range of intermediate cases) on the same fundamental footing.

Kumar and Sorbello[11] have shown how this may be formally accomplished through the use of linear-response theory. This theory expresses the response of the electrons to the applied electric field in terms of correlation functions of the system in the absence of the field. It only requires that the response be linear in the applied field, which is true since the metals are ohmic. However the evaluation of the formal expressions is in general quite difficult and one is soon forced into an approximate model and/or evaluation. Kumar and Sorbello invoked an approximate bootstrap argument to recast their general expressions into more tractable form.[11,12] We have given a rigorous basis for this transformation to random-force correlation functions[10] but found that its correct evaluation is just as difficult as that for the original expressions. One hopeful fact that did emerge from this work was that we can reproduce most of the modern quantitative theories[13-18] merely by assuming that the electrons in the system move as independent particles among the array of ion scatterers. Of course, the precise electron-ion potential has the requirement of self-consistency, but this is a restriction that can be determined in the system unperturbed by the electric field. The success of this simple approximation motivated the present paper.

An independent-particle treatment of the electron dynamics, in fact, does allow considerable progress. Although we must still assume that the net scattering in the system is weak, our results show how one can easily go beyond a Born approximation for the driving force.[15-20] Furthermore, we show that there is no theoretical need to consider only an average driving force: Our final expressions depend on the actual locations of the electromigrating atom and all its neighbors. The derivation of these formulas is given in Sec. II. In Sec. III we discuss some of the implications of our results and their possible extension. We also discuss the work of Sham,[21] which parallels and complements this paper.

In the remainder of this section we wish to give a simple physical description of our results based on the Boltzmann equation. This discussion will also allow one to see clearly how our results resolve the controversy over the existence and quantitative significance of the so-called Landauer resistivity dipole contribution[22] to the driving force of electromigration.[7,23,24]

Our use of the Boltzmann equation means that we are focusing on the response of electrons in the conduction band and are not considering the polarization response of the more tightly bound electrons. Hence we consider the electron-ion potential to be the appropriately screened interaction between an electron and ions of charge Z, where Z is the valence, and assume that the net effect of such interactions is only to give the electrons a long mean free path. The long mean free path does not, however, imply that the electron states are nearly plane waves. The electron states are in general severely distorted in the immediate vicinity of each ion; it is only their net scattering rate from the ion configuration which is weak. This situation is the familiar basis of pseudopotential theory.

To put our use of the Boltzmann equation in context, let us consider briefly the approach of previous workers. The early ballistic theories[13,14] of the electron-wind force determine this force directly from the Boltzmann equation,

$$e v_\nu(\vec{k}) \frac{\partial n_0}{\partial \epsilon} E_\nu = \frac{\partial n}{\partial t}\bigg|_{\mathrm{coll}} \approx -\frac{n_1}{\tau} , \tag{1}$$

where $\vec{E}$ is the uniform applied electric field; $n = n_0 + n_1$ is the electronic distribution function, with n_0 independent of $\vec{E}$ and n_1 linear in $\vec{E}$; $\vec{v}$ is the velocity of an electron of state label $\vec{k}$ and energy ϵ; and $e < 0$ is the electron's charge. We use the Einstein convention to imply a sum over repeated Cartesian subscripts. In the second line we have approximated the collision integral by its relaxation-time form, which is sufficient for our discussion here. The ballistic theories assert that the wind force on an ion is proportional to the negative time rate of change of $\vec{k}$ due to collisions with that ion. This approach soon encounters ambiguities in extracting the portion of the collision operator (or the portion of $1/\tau$) that may be considered as due to a certain ion, especially when multiple scattering is important. Such ambiguities are avoided in the approach of Bosvieux and Friedel.[15] They concentrate on calculating the induced charge density about the ions and from that, by the Hellman-Feynman theorem, calculate the induced force on any particular ion. Their approach was extended by Gerl[16] and made quantitative through the use of pseudopotentials by Sorbello.[18] However, in all these papers the induced electron density is calculated by quantum mechanics only to linear order in the electron-ion potential strength. There is a similar approximation in the classical analysis of Das and Peierls.[8] Consequently these theories, as written, cannot describe any contribution to the driving force arising from the induced charge densities of higher order in the scattering strength. Such a higher-order contribution was proposed by Landauer as a consequence of his theory of impurity resistivity,[22] wherein dipolar charge distributions proportional to the resistivity were found to develop in the presence of conduction about each impurity scattering center. Landauer and Woo[23] made a rough estimate of the size of such effects on the driving force. They found it comparable to the Bosvieux-Friedel term, the higher order in the scattering strength being compensated by the nonoscillatory nature of the charge density.[23] One need not however carry out such an order by order calculation of contributions.

To develop a more useful procedure we use the Boltzmann equation in the spirit of the Bosvieux-Friedel approach; i.e., we compute the induced charge density from the Boltzmann equation assuming that only the distribution function is modified by the electric field. Since the induced change in the electron-density matrix is diagonal in $\vec{k}$ and equal to $n_1(\vec{k})$, we find simply

$$\delta n(\vec{r}) = e \sum_{\vec{k}} n_1(\vec{k}) \, |\psi_{\vec{k}}(\vec{r})|^2 , \tag{2}$$

where $\psi_{\vec{k}}(\vec{r})$ is the wave function associated with state label $\vec{k}$ and $\delta n(\vec{r})$ is the induced charge density. Our general result has essentially this form, the only subtlety involved lies in the recipe for determining $|\psi_{\vec{k}}(\vec{r})|^2$. We only emphasize here that it is independent of the electric field; the appropriate recipe is derived in Sec. II.

For now let us just consider a simple case where we may guess the answer: A dilute random array of spherically symmetric impurities in jellium. To compute the indirect contribution to the driving force for this case we only need the induced charge density about the impurity ion in question. Around each impurity we expect $\psi_{\vec{k}}(\vec{r})$ to be well approximated by $\psi^{+}_{\vec{k}}(\vec{r})$, the scattered-wave solution about that impurity. Far outside the range of the ion potential this wave function may be written[25]

$$\psi_{\vec{k}}^{+}(\vec{r}) \to e^{i\vec{k}\cdot\vec{r}} + f(\theta)\, e^{ikr}/r \;, \tag{3}$$

where θ is the angle between $\vec{k}$ and $\vec{r}$ and the impurity is at $\vec{r}=0$. To obtain the asymptotic form of $\delta n(\vec{r})$ we simply substitute (3) into (2) and use the solution of (1) appropriate for this model:

$$n_1(\vec{k}) = \left(-\frac{\partial n_0}{\partial \epsilon}\right)\frac{\hbar k_\nu}{m}\, eE_\nu \tau \;, \tag{4}$$

where m is the electron mass, and at zero electron temperature $(-\partial n_0/\partial\epsilon) = \delta(\epsilon - \epsilon_F)$, with ϵ_F the Fermi energy. Further in calculating $|\psi_{\vec{k}}(\vec{r})|^2$, we replace the plane wave by its asymptotic form,[25]

$$e^{i\vec{k}\cdot\vec{r}} \to (2\pi/ikr)\left[\delta(\hat{\vec{k}}-\hat{\vec{r}})\, e^{ikr} - \delta(\hat{\vec{k}}+\hat{\vec{r}})\, e^{-ikr}\right] + O(1/r^2). \tag{5}$$

After some straightforward algebra, which requires the use of the optical theorem,[25]

$$\mathrm{Im} f(0) = \frac{k}{4\pi}\int d\Omega\, |f(\theta)|^2 \;, \tag{6}$$

where Im denotes "imaginary part of" and the integral is over solid angle, we find

$$\delta n(\vec{r}) \to 3\hat{\vec{E}}\cdot\hat{\vec{r}}\,\bar{n}\left(\frac{-eE\tau}{\hbar k_F}\right)\left(\frac{1}{k_F r^2}\,\mathrm{Im}\left[f(\pi)\, e^{2ik_F r}\right] + \frac{1}{r^2}\int\frac{d\Omega}{4\pi}(1-\cos\theta)|f(\theta)|^2\right) + O(1/r^3) \;, \tag{7}$$

where $\bar{n}$ is the average charge density, k_F is the Fermi momentum, and $f(\pi)$ is the backscattering amplitude. Although the specific result (7) is only valid at large r, it clearly shows the existence of both oscillatory[16] and monotonic contributions to $\delta n(\vec{r})$.[22] Note that the transport cross section multiplies the monotonic term; this is the dipolar charge distribution that gives rise to the Landauer resistivity dipole.[22] One can easily write down formulas for $\delta n(\vec{r})$ valid for all $\vec{r}$ in terms of the radial solutions of the electron Schrödinger equation.[25] We do not give these here because our interest is in the driving force which involves an integral over $\delta n(\vec{r})$. By using the formal definition of $\psi_{\vec{k}}^{+}(\vec{r})$ we show in Sec. II that the relevant integral can be expressed in terms of

$$\frac{1}{\tau_i} = \frac{2\pi}{\hbar}\sum_{\vec{k}'}|\langle\vec{k}|\,t_i\,|\vec{k}'\rangle|^2(1-\hat{\vec{k}}\cdot\hat{\vec{k}}')\,\delta(\epsilon_F - \epsilon_{\vec{k}'}) \;, \tag{8}$$

where the $\langle\vec{k}|\,t_i\,|\vec{k}'\rangle$ are plane-wave matrix elements of the t matrix of the impurity ion and $\vec{k}$ is a vector of length k_F. The remarkable feature is that (8) differs from the Bosvieux-Friedel (Born-approximation) result only in the replacement of the electron-ion potential v_i by t_i. The formula agrees exactly with the prediction of the ballistic theories,[13,14] since our dilute-impurity model is the one for which they encounter no ambiguities.

From the above simple considerations we can draw the following conclusions: First, there is a contribution to the indirect driving force of electromigration from the Landauer resistivity dipoles. Second, the question of the quantitative significance of this contribution and higher-order ones is not particularly relevant. By this we mean that, since one only measures the net driving force and since this is by (8) expressible in terms of a t matrix, the size of higher-order corrections to the Born approximation for the above model will depend on how close plane-wave matrix elements of v_i approximate those of t_i. Since the spirit of pseudopotential theory is to make these differences as small as possible, we see that by choosing a "good" pseudopotential we can effectively eliminate all but the Born-approximation term from our final result.

II. DERIVATION

In this section our aim is to derive the formulas which justify the simple description we have just given. The quantity we seek is the indirect contribution to the driving force; i.e., the one due to the electron's response to the applied field. We do assume that the net scattering in our system is weak in order that we might hope to make contact with the Boltzmann equation, which is only justified in this limit. Hence our attention is on the conduction electrons, and we cannot describe the purely polarization response of tightly bound electrons. By assuming that the electron-ion potential is an appropriately screened interaction corresponding to ions of valence Z, we formally eliminate the core electrons from consideration. This reasonable but somewhat arbitrary procedure, which presumes that there is a clear distinction between conduction and core electrons, leaves us with a "direct" driving force of $-Ze\vec{E}$. Here and below $\vec{E}$ is the average macroscopic field in the sample.[10]

The other major assumption we make is to treat the electrons as independent particles moving among a self-consistently screened array of ion potentials. Since the linear-response formulas we use relate the indirect driving force only to properties of the system before the application of the electric field, our procedure amounts to the common assumption of metal physics that electron dynamics may be adequately described by the dynamics of independent quasiparticles. We have already noted its success in low-order calculations[10] and shall discuss its justification further in Sec. III.

For simplicity we assume that the electron temperature is zero, no magnetic field is present, and all electron scattering may be treated as elastic. This last assumption is a consequence of the Born-

Oppenheimer approximation; note that it does not eliminate phonon scattering.[10,18,26] In discussing our formulas the model system we have in mind is a liquid metal. This avoids consideration of band-structure effects. However our formulas have been written so that they would also apply to a one-band model of a crystal; i.e., a model which neglects any interband coupling. We return to this point in Sec. III.

Let us begin with the linear-response formula for the indirect driving force on a particular ion,[10,11,27] which we denote by $f_{\mu\nu}E_\nu$ where $f_{\mu\nu} = \lim_{\omega\to 0} f_{\mu\nu}[\omega]$:

$$f_{\mu\nu}[\omega]=\frac{1}{i\hbar}\int_0^\infty d\tau\, e^{i\omega\tau}\langle[f_\mu(\tau),\, -eR_\nu]\rangle \tag{9a}$$

$$=\frac{1}{\hbar\omega}\int_0^\infty d\tau\, e^{i\omega\tau}\langle[f_\mu(\tau),\, J_\nu]\rangle \;. \tag{9b}$$

Here $\vec{f}$ is the operator of the force on the ion in question, $\vec{J}$ is e times the total-velocity operator, and $e\vec{R}$ is the dipole operator of the electron system: $e(\partial/\partial t)\vec{R}=\vec{J}$. The time dependence of $\vec{f}$ is determined by the adiabatic Hamiltonian H as is the ensemble average denoted by the angular brackets. The square brackets denote a commutator. To pass from (9a) to (9b) requires simply an integration by parts. Next we use the formalism of second quantization and our assumption of independent electrons to reduce (9b) to

$$f_{\mu\nu}[\omega]=\frac{i}{\omega}\sum_{a,b}\frac{n_a-n_b}{\epsilon_a+\hbar\omega-\epsilon_b+i0^+}\langle a|f_\mu|b\rangle\langle b|J_\nu|a\rangle \;, \tag{10}$$

where the labels a, b refer to single-particle electron eigenstates (of energy ϵ_a, ϵ_b and wave function $|a\rangle$, $|b\rangle$), and the n's are state-occupation factors, which at zero electron temperature become

$$n_a=\begin{cases}1, & \epsilon_F>\epsilon_a \;,\\ 0, & \epsilon_F<\epsilon_a \;,\end{cases} \tag{11}$$

where ϵ_F is the Fermi energy. We remark that in zero magnetic field the wave functions may be chosen as real functions so that the product of matrix elements in (10) is a pure imaginary number. Consequently, the real part of $f_{\mu\nu}$ is given by the principal value part of the summation. This implies that in general $f_{\mu\nu}$ is not determined solely by properties of electrons at the Fermi level. This situation is in contrast to that for the electrical conductivity $\sigma_{\mu\nu}$ where f_μ is replaced by J_μ in the expression (10), and one soon arrives at the Greenwood-Kubo-Peierls formula.[27,28] The physics in these remarks are that the possible polarization response of core electrons is still contained in (10). It is only when we make an approximate evaluation of (10) based on weak net scattering that the response of electrons away from the Fermi level will be suppressed.

To this end we introduce into (10) the identity

$$i\,\frac{n_a-n_b}{\epsilon_a+\hbar\omega-\epsilon_b+i0^+}=\int_{-\infty}^{\infty}\frac{d(\hbar\bar{\omega})}{2\pi}\,G_b(\omega+\bar{\omega})\,G_a(\bar{\omega}) \;, \tag{12}$$

where the G's are simple Green's functions

$$G_a(\bar{\omega})=\langle a|\,G(\bar{\omega})\,|a\rangle=[\hbar\bar{\omega}-\epsilon_a+i0^+\operatorname{sgn}(\hbar\bar{\omega}-\epsilon_F)]^{-1} \;. \tag{13}$$

Then we remove the explicit state sums to express $f_{\mu\nu}[\omega]$ in terms of a single-particle trace

$$f_{\mu\nu}[\omega]=\frac{1}{\omega}\int_{-\infty}^{\infty}\frac{d(\hbar\bar{\omega})}{2\pi}\,\mathrm{Tr}\,[f_\mu G^\alpha(\omega+\bar{\omega})J_\nu G^\beta(\bar{\omega})] \;, \tag{14}$$

where the extra index on the $G(\bar{\omega})$ is ± depending on whether $\hbar\bar{\omega}\gtrless\epsilon_F$, and similarly for the index on $G(\omega+\bar{\omega})$. Now we make an infinite-order expansion of each G in powers of the electron-ion potential V; e.g.,

$$G^\beta(\bar{\omega})=G_0^\beta(\bar{\omega})\sum_{n=0}^{\infty}[VG_0^\beta(\bar{\omega})]^n \;, \tag{15}$$

and seek a resummation. By this method we are following the work of Langer on the impurity resistance problem,[29,30] especially its extension to treat liquid metals.[31] We have not introduced the projection operators of Ref. 10 since they only complicate the resummation; their utility lies more in formal applications.

At this point in the theory one has always introduced plane-wave intermediate states and taken an average over the configuration of scattering centers.[29–32] As we have already discussed[10] such a procedure is, however, most undesirable in the calculation of the electromigration driving force. We can circumvent this averaging process by the following arguments and assumptions. The resummation is made possible by the appearance of the Van Hove diagonality conditions[33,34] in the plane-wave expansion.[32] To obtain these without a configuration average we need to assume, first, that the disorder in the system is homogeneous and, second, that any short-range order is limited in spatial extent by a microscopic length r_c (correlation length) and that the spatial extent of the influence of any one ion on V is similarly limited to a microscopic length r_p. If we were to write the electron-ion potential at $\vec{x}$ as a superposition $V(\vec{x})=\sum_i v_i(\vec{x}-R_i)$, where the sum runs over ion locations $\{\vec{R}_i\}$, then our assumptions are merely that the array of $\{\vec{R}_i\}$ is homogeneously disordered (no long-range order) and that the range of any v_i is microscopic. Hence these assumptions are easily met. Their utility lies in the fact that from them we may deduce

$$\frac{1}{\Omega}\int d\,\vec{x}'\,S(\vec{x}')\,e^{i\vec{q}\cdot\vec{x}'}=\langle\langle S(\vec{x})\rangle\rangle\,\delta_{\vec{q},0}+O\!\left(\frac{1}{\Omega}\right), \tag{16}$$

where Ω is the volume of the system and $S(\vec{x})$ is any function that depends only on the configuration of ions within the distance L of $\vec{x}$, where $L \ll \Omega^{1/3}$. The double angular brackets denote a configuration average; hence, $\langle\langle S(\vec{x})\rangle\rangle$ is independent of $\vec{x}$. In essence (16) replaces a space average by a configuration average, but only for the diagonal fragment. To see that functions such as $S(\vec{x})$ do arise in our infinite-order expansion of (14) consider, for example,

$$\langle k | G_0^\alpha V G_0^\alpha V G_0^\alpha V G_0^\alpha V | k' \rangle = \frac{1}{\Omega} \int dx\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{x}} S_1(\vec{x}) \,, \tag{17a}$$

or

$$\langle k | G_0^\alpha V G_0^\alpha J_\nu G_0^\beta V G_0^\beta V G_0^\beta V G_0^\beta | k' \rangle = \frac{1}{\Omega} \int d\vec{x}\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{x}} S_2(\vec{x}) \,, \tag{17b}$$

where $|\vec{k}\rangle$ and $|\vec{k}'\rangle$ are plane-wave states. When we insert complete sets of intermediate momentum states and sum over them, these expressions will be effectively coarse-grain averaged with respect to momentum,[32,35,36] which in turn makes them satisfy the conditions above on S and, furthermore, makes their configuration average well-defined.[32,35] Note, however, that in

$$\langle k | G_0^\beta V G_0^\beta f_\mu G_0^\alpha V G_0^\alpha | k' \rangle = \frac{1}{\Omega} \int d\vec{x}\, e^{-i(\vec{k}-\vec{k}')\cdot\vec{x}} S_3(\vec{x}) \,, \tag{18}$$

the presence of f_μ and the existence of r_p means that $S_3(\vec{x})$ does not satisfy the conditions for (16). Consequently, $S_3(\vec{x})$ cannot be replaced by its average and does depend on the specific environment of the electromigrating ion of concern.

Since the appearance of the δ function in (16) constitutes in essence the Van Hove diagonality conditions,[32–34] we can immediately effect a resummation. Since J_ν is diagonal in momentum space, we find

$$f_{\mu\nu}[\omega] = \frac{1}{\omega} \int_{-\infty}^{\infty} \frac{d(\hbar\bar{\omega})}{2\pi} \sum_{\vec{k}} \Pi_\nu^{\alpha\beta}(\vec{k}) \mathcal{V}_\mu^{\beta\alpha}(\vec{k}) \,, \tag{19}$$

where the vertex is given by

$$\mathcal{V}_\mu^{\beta\alpha}(\vec{k}) = \left(\langle \vec{k} | \sum_{n=0}^{\infty} (V g^\beta)^n f_\mu \sum_{m=0}^{\infty} (g^\alpha V)^m | \vec{k} \rangle \right)_{\text{i.d.}} \,, \tag{20}$$

with $g^\alpha = \langle\langle G^\alpha \rangle\rangle$, and the weighting factor is

$$\Pi_\nu^{\alpha\beta}(\vec{k}) = \langle\langle(\langle k | G^\alpha J_\nu G^\beta | k \rangle)\rangle\rangle \,. \tag{21}$$

The i.d. restriction in (20) denotes "irreducible diagonal"[33,34] and means that $\mathcal{V}_\mu(\vec{k})$ is to be evaluated by inserting sets of plane waves in the expansion of (20), but that in the summations none of the labels of matrix elements of V can equal $\vec{k}$ or each other. These restrictions arise because the resummation procedure to obtain (19) has removed the diagonal singularities.

To further reduce and interpret (19) let us first consider $\Pi_\nu^{\alpha\beta}(\vec{k})$. This quantity satisfies a Bethe-Salpeter equation,[29,30,33,34] which in the weak net-scattering limit becomes the Boltzmann equation of (1). This limit is obtained if we assume

$$\langle \vec{k} | g^\beta | \vec{k} \rangle = [\hbar\bar{\omega} - \epsilon_{\vec{k}} + i\Gamma_{\vec{k}} \operatorname{sgn}(\hbar\bar{\omega} - \epsilon_F)]^{-1} \,, \tag{22}$$

with $\Gamma_{\vec{k}}/\epsilon_F \ll 1$. Here $\hbar/(2\Gamma_{\vec{k}}) = \tau_{\vec{k}}$ is essentially the lifetime of the state $\vec{k}$. We shall assume that g has the form (22) for all $\vec{k}$ and $\bar{\omega}$, but the only check considered to apply is to be sure that the electron lifetime at the Fermi level is long. Furthermore we only retain $\Pi_\nu^{+-}(k)$ since the other terms give contributions of $O(\Gamma_{k_F}/\epsilon_F)$ if (22) holds. We remark that it is these specific procedures that suppress the response of electrons away from the Fermi level; we hope to return to this point in later work. Granted the imposition of the weak net-scattering limit, we find that $\Pi_\nu^{+-}(k)$ obeys[29,30]

$$\frac{\hbar}{2\pi} \Pi_\nu^{+-}(\vec{k}) = \tau_{\vec{k}}\, \delta(\epsilon_{\vec{k}} - \epsilon_F) \times \left(\langle \vec{k} | J_\nu | \vec{k} \rangle + \sum_{\vec{l}} \frac{2\pi}{\hbar} W^{+-}(\vec{k}, \vec{l}) \frac{\hbar}{2\pi} \Pi_\nu^{+-}(\vec{l}) \right) , \tag{23}$$

where

$$W^{+-}(\vec{k}, \vec{l}) = \left(\langle \vec{k} | V \sum_{n=0}^{\infty} (g^+ V)^n | \vec{l} \rangle \langle \vec{l} | V \times \sum_{m=0}^{\infty} (g^- V)^m | \vec{k} \rangle \right)_{\text{i.d.}} \,, \tag{24}$$

and by the generalized optical theorem[33,34] (in the weak net-scattering limit[31])

$$\frac{1}{\tau_{\vec{k}}} = \sum_{\vec{l}} \frac{2\pi}{\hbar} W^{+-}(\vec{k}, \vec{l})\, \delta(\epsilon_{\vec{k}} - \epsilon_{\vec{l}}) \,. \tag{25}$$

Substituting this result in (23) we find after a simple rearrangement

$$-\delta(\epsilon_{\vec{k}} - \epsilon_F) \langle \vec{k} | J_\nu | \vec{k} \rangle = \sum_{\vec{l}} T(\vec{k}, \vec{l}) \left(\frac{\hbar}{2\pi} \Pi_\nu^{+-}(\vec{l}) - \frac{\hbar}{2\pi} \Pi_\nu^{+-}(\vec{k}) \right) , \tag{26}$$

with the transition operator given by

$$T(\vec{k}, \vec{l}) = T(\vec{l}, \vec{k}) = (2\pi/\hbar) W^{+-}(\vec{k}, \vec{l})\, \delta(\epsilon_{\vec{k}} - \epsilon_{\vec{l}}) \,. \tag{27}$$

In all these expressions, (20) and (23)–(27), we have set $\omega = 0$ due to the eventual limiting requirement on $f_{\mu\nu}[\omega]$; the $1/\omega$ in (19) is simply cancelled by the $\bar{\omega}$ integral in the weak net-scattering limit as $\omega \to 0$. Comparing (26) with (1) we identify

$$(\hbar/2\pi)\, \Pi_\nu^{+-}(\vec{k}) E_\nu = n_1(\vec{k}) \,, \tag{28}$$

which reduces (19) after the $\bar{\omega}$ integral to

$$f_{\mu\nu}E_\nu = \sum_{\vec{k}} n_1(\vec{k})\mathcal{V}^{-+}_\mu(\vec{k}) \;, \tag{29}$$

the analog of (2).

To make this connection clear we must examine $\mathcal{V}^{-+}_\mu(\vec{k})$. We expect it to be similar to $\int d\vec{x}\,|\psi_{\vec{k}}(\vec{x})|^2 \times f_\mu(\vec{x})$, where $f_\mu(\vec{x})$ is the contribution to the force on the ion of concern by electrons at $\vec{x}$. In fact such structure is apparent in (20), which may consequently be interpreted as giving the precise recipe for $|\psi_{\vec{k}}(\vec{x})|^2$. Unfortunately this recipe is in terms of the "i.d." restriction which is only interpretable in a momentum-space expansion. Also (20) shows that only $|\psi_{\vec{k}}(\vec{x})|^2$ is rigorously defined not $\psi_{\vec{k}}(\vec{x})$ alone. To develop an approximate recipe that is more tractable, consider various limits of (20). First if we simply expand $\mathcal{V}^{-+}_\mu(\vec{k})$ in powers of the electron-ion potential, the first nonvanishing term is at second order, the Bosvieux-Friedel result

$$\mathcal{V}^{-+}_\mu(\vec{k}) \cong \sum_{\vec{k}'(\neq\vec{k})} [\langle\vec{k}|\,V|\vec{k}'\rangle\, G^-_0(\vec{k}')\,\langle\vec{k}'|f_\mu|\vec{k}\rangle + \langle\vec{k}|f_\mu|\vec{k}'\rangle\, G^+_0(\vec{k}')\,\langle\vec{k}'|\,V|\vec{k}\rangle] \;. \tag{30}$$

Here to be consistent with the weak-scattering limit we have replaced $g^\pm \rightarrow G^\pm_0$. Equation (30) certainly has the appearance of a perturbative estimate of $|\psi_{\vec{k}}|^2$, retaining only the first-order interference terms.[15,16,18,22] A more revealing model is the one discussed in the introduction, a dilute array of impurities. In order to evaluate (20) for this model, note that the diagonal fragments that would arise in (20) if we ignored the "i.d." restriction all involve factors of the impurity-ion density.[29,30,35] Thus in the low-density limit we can consistently evaluate $\mathcal{V}^{-+}_\mu(\vec{k})$ if we replace V by v_i, the potential due only to the ion of concern, and ignore the "i.d." restriction. We then find (*d* for dilute)

$$\mathcal{V}^{-+}_{\mu,d}(\vec{k}) = \langle\vec{k}|(1+t^-_i G^-_0)f^i_\mu(G^+_0 t^+_i + 1)|\vec{k}\rangle$$

$$= \int d\vec{x}\,|\psi^+_{\vec{k},i}(\vec{x})|^2 f^i_\mu(\vec{x}) \;, \tag{31}$$

where t_i is the ion's t matrix, and we have used the formal definition of the outgoing wave-scattering state[25]: $\psi^+_{\vec{k},i}(\vec{x}) = \langle\vec{x}|(1+G^+_0 t^+_i)|\vec{k}\rangle$. Thus we confirm our intuitive guess of Sec. I.

Although at present we can find no other limits which we can treat exactly and must therefore in general rely only on the prescription (20), the second model treated above does suggest a useful cluster approximation. To compute the force on a particular ion we only need the wave function in the near ($\sim r_p$) vicinity of that ion. The mean free path is, in the weak net-scattering limit, much longer than this distance. Thus we argue that a reasonable calculation of the relevant portion of the wave function can be done by including only the scattering from ions in the near vicinity of the ion in question. We thus retain the possibly strong reactive scattering that distorts the wave function about each ion, but suppress the weak dissipative scattering that leads to a loss of phase coherence over a mean free path. In terms of (20) we are proposing that one take for V the electron-ion potential due to a cluster of ions about the one in question, with the dimension of this cluster being somewhat greater than r_p but much less than the mean free path. One omits all other ion scatterers and neglects the i.d. restriction in (20). This is the prescription in a liquid metal; in a crystal, one would remove all defects outside of the cluster but retain the perfect-lattice scattering in order to preserve the Bloch waves. Of course to be reasonable the results must not depend sensitively on the cluster size. In the absence of detailed calculations (aside from the results of Sorbello,[18] which support this picture), it is difficult to assess the precise validity of this cluster approximation. However, examination of the effect of this approximation on the momentum expansion of (20) is encouraging. The internal sums in (20) over the unrestricted intermediate momentum states are, by the effective coarse-grain average[32] and phase cancellation, functions only of the local potential about the ion in question. Furthermore, the diagonal fragments in the cluster evaluation of (20), though they do not vanish, are not δ functions since the integrals such as (17a) have no contribution far away from the cluster. Their restricted region in phase space and now finite contribution suppress their importance, in effect applying the i.d. restriction. These arguments suggest that a cluster evaluation of (20) is a reasonable approximation.

If we accept this approximation, then the removal of the i.d. restriction allows us certain useful formal manipulations. Just as in (31) we can now write (*c* for cluster)

$$\mathcal{V}^{-+}_{\mu,c}(\vec{k}) = \langle\vec{k}|(1+T^-_i G^-_0)f_\mu(G^+_0 T^+_i + 1)|\vec{k}\rangle$$

$$= \int d\vec{x}\,|\Psi^+_{\vec{k},i}(\vec{x})|^2 f_\mu(\vec{x}) \;, \tag{32}$$

where T_i is the t matrix of the cluster about ion i and $\Psi^+_{\vec{k},i}(\vec{x})$ is the outgoing wave-scattering state for this cluster. The direct calculation of $\Psi^+_{\vec{k},i}(\vec{x})$ is easily within the scope of existing multiple-scattering theory, say for a muffin-tin model of the electron-ion potential.[37,38] However, it is only an integral over $|\Psi^+_{\vec{k},i}(\vec{x})|^2$ that enters in the electromigration problem. This integral may be simplified as shown in the Appendix. Using the fact $n_1(\vec{k}) = -n_1(-\vec{k})$, the only part of $\mathcal{V}^{-+}_{\mu,c}(\vec{k})$ that contributes to (29) is

$$\mathcal{V}^{-+}_{\mu,c}(\vec{k}) = 2\pi i \sum_{\vec{l}} \left(\frac{\partial}{\partial R^i_\mu} \langle \vec{k} | T^-_i | \vec{l} \rangle \right) \delta(\epsilon_{\vec{k}} - \epsilon_{\vec{l}}) \langle \vec{l} | T^+_i | \vec{k} \rangle \,, \tag{33}$$

where R^i_μ is the μth Cartesian component of the position vector of the ith ion. This result is easily evaluated for the model of dilute impurities in jellium since then

$$\langle \vec{k} | t_i | \vec{l} \rangle = \langle \vec{k} | t_i | \vec{l} \rangle_0 \, e^{-i(\vec{k}-\vec{l})\cdot\vec{R}^i} \,, \tag{34}$$

where $\langle \vec{k} | t_i | \vec{l} \rangle_0$ is the matrix element of the single-ion t matrix when it is at the origin. Substituting in the dilute limit of (33) yields

$$\begin{aligned} \mathcal{V}^{-+}_{\mu,d}(\vec{k}) &= +\, 2\pi \sum_{\vec{l}} |\langle \vec{k} | t_i | \vec{l} \rangle|^2 (k_\mu - l_\mu)\, \delta(\epsilon_{\vec{k}} - \epsilon_{\vec{l}}) \\ &= \hbar k_\mu \left(\frac{2\pi}{\hbar} \sum_{\vec{l}} |\langle \vec{k} | t_i | \vec{l} \rangle|^2 (1 - \hat{k}\cdot\hat{l})\, \delta(\epsilon_{\vec{k}} - \epsilon_{\vec{l}}) \right) \\ &= \hbar k_\mu \left(\frac{1}{\tau_i} \right) , \end{aligned} \tag{35}$$

where the second line follows for the case of spherical symmetry of t_i and the third line from a comparison with (8) and a recollection that (29) will force $|\vec{k}| = k_F$. Finally, using (1) to find $n_1(\vec{k})$, (29) gives the standard result for this model.[13,14]

III. DISCUSSION

In this section we wish to restate our results in general terms, pointing out some of their implications and limitations. We have obtained, as expressed in (20) and (29), a complete solution of the problem we set for ourselves. With the assumption that the electrons may be treated as independent, undergoing a weak net scattering from the ion potentials, Eq. (29) is the prescription for calculating the indirect contribution to the driving force of electromigration. It consists of two factors. The first $n_1(\vec{k})$ is a property of the average system, independent of any particular ion. We have not written out a formula for $n_1(\vec{k})$ because we wish to leave it simply as a solution of the relevant Boltzmann equation of the system. In this way our treatment may be immediately generalized to other perturbations beside an electric field; say, for instance, a temperature gradient. On the other hand, the second factor in (29), $\mathcal{V}^{-+}_\mu(\vec{k})$, is a quantity that is specific to the ion in question and its local environment.[39] We have shown, either in limiting cases or by a reasonable cluster approximation, how to evaluate this vertex. In order to do an actual calculation of the driving force, one must determine V, the self-consistent electron-ion potential. We emphasize that this preliminary effort is to be done on the system unperturbed by the electric field. This feature is a principal advantage of the linear-response formalism.

Turning to our approximations, we remark that the assumption of weak net scattering has, to a certain extent, fixed the form of our final result, wherein it is only the distribution of electron states that is modified by the field, not the states themselves.[15] This is a reasonable result for electrons that obey a Boltzmann equation, but not all electrons follow such dynamics. Consequently our separate treatment of the direct plus polarization-indirect force (i.e., $-ZeE_\mu$) and the wind-indirect force [i.e., (29)] is suspect. We have in effect said that an electron in an applied field either polarizes or conducts. Some sort of intermediate behavior would seem possible,[9,15] but we presently don't know how to describe it.

Our second major assumption, the use of independent-electron dynamics, has been recently examined by Sham.[21] Although he limits his treatment to a dilute system of impurities, he does use the full quantum-field theory to examine the consequences of electron-electron interactions. His result for the driving force on one of the dilute impurities is essentially our Eq. (29) with the substitution of (35) for the vertex. The slight difference rests in the fact that $n_1(\vec{k})$ is now the solution of the Landau-Boltzmann equation, which allows for Fermi liquid effects.[40] The mutual interaction of the electrons that he includes merely acts to convert the "bare" electron-ion potential to a self-consistently screened interaction so that the vertex is the same as our result. Of course one now has a complete diagrammatic prescription for this interaction.[21] Furthermore it seems that a similar proof of the essential validity of our independent-particle treatment is possible for a general array of scattering centers. The key point, in field-theoretic language,[21] is the separation of the force vertex from the current vertex in the evaluation of (9). That ensures a result of the form (29), wherein the distribution for the electrons is determined independently of the details of the potential about the electromigrating atom, which is described by $\mathcal{V}^{-+}_\mu(\vec{k})$. The existence of this separation only requires the general assumptions that lead to the Van Hove diagonality conditions.

We consider next whether our result is consistent with the general sum rule,[10]

$$\sum_i f^i_{\mu\nu} E_\nu = NeE_\mu \,, \tag{36}$$

where the sum on i runs over all ions and N is the number of electrons in the system. For this we need to examine the sum of $\mathcal{V}^{-+}_\mu(k)$ over all scatterers. To simplify matters assume that the total electron-ion potential may be written as a linear superposition of local potentials, v_i associated with the ith scatterer. Then, explicitly limiting ourselves for the moment to a liquid metal, we have, since the $|\vec{k}\rangle$ are plane waves,

$$\langle \vec{k}|f^i_\mu|\vec{k}'\rangle = -\frac{\partial}{\partial R^i_\mu}\langle \vec{k}|v_i(\vec{r}-\vec{R}^i)|\vec{k}'\rangle$$

$$= i(k_\mu - k'_\mu)\langle \vec{k}|v_i|\vec{k}'\rangle \ , \tag{37}$$

where $\vec{r}$ and $\vec{R}^i$ are the electron and ion coordinates, respectively. If we sum (29) over all scatterers using (37) we obtain

$$\sum_{\substack{\text{all}\\ \text{scatterers}}} f^i_{\mu\nu}E_\nu = N_{\mu\nu}eE_\nu \tag{38a}$$

$$= \left((1/e)\sum_{\vec{k}}\delta(\epsilon_F-\epsilon_k)\hbar k_\mu\langle\vec{k}|J_\nu|\vec{k}\rangle\right)eE_\nu \ . \tag{38b}$$

The exact sum rule (36) requires this result to be NeE_μ; consequently the dimensionless tensor $N_{\mu\nu}$ defines our model's estimate of N. In a weak net-scattering liquid metal we immediately find that $N_{\mu\nu}=N^c\delta_{\mu\nu}$, with N^c the number of conduction electrons. This result is consistent with our approximation of removing the tightly bound core electrons from explicit consideration and simultaneously reducing the direct-force term for any ion from $-Z^beE_\mu$ to $-ZeE_\mu$, where Z^b is the bare charge of the nucleus and Z is its valence in the metal. In effect this procedure of treating the (supposed) pure polarization response has removed a contribution $(N-N^c)eE_\mu$ from the sum in (36). For a liquid-metal system this approach is well-defined and consistent in the weak net-scattering limit.

Lastly, we wish to discuss some aspects of the influence of band structure on the driving force. Our work here has not come to full grips with this problem, even within our major assumptions. We have written out the derivation in Sec. II so that it would be valid for a one-band model of a metal; there was no need to mention the band dispersion. Hence our results should be valid for a crystal whose conduction bands may be treated in parallel and in a weak net-scattering limit. In fact if we generalize this last assumption we can even include interband scattering as long as the various bands at any $\vec{k}$ are well separated in energy. Mathematically this is made possible by the use of $\Gamma_{\vec{k}}/(\epsilon^n_{\vec{k}}-\epsilon^{n'}_{\vec{k}})$, as well as $\Gamma_{\vec{k}}/\epsilon_F$, as a small parameter. Here $\epsilon^n_{\vec{k}}$ and $\epsilon^{n'}_{\vec{k}}$ are the energies for state $\vec{k}$ in bands n and n', respectively. One may consider this restriction as part of the requirements of a general weak net-scattering limit; they are necessary for one to derive the usual Boltzmann equation. Within these limitations our formulas may be applied to crystals.

To point out some of their subtlety, let us consider their implication in regard to (36). We immediately encounter the difficulty that (37) will not in general be true in a crystal. Only in an effective-mass approximation,[21,41] when one has a small Fermi surface near a single-band extremum, can one obtain (37). Consequently we can only check the sum rule in this limit, but even here it is revealing. Given (37) in a crystal, we may pass with no further approximation, aside from that of weak net scattering between Bloch waves, to (38). Note that now[42]

$$\frac{1}{e}\langle n\vec{k}|J_\nu|n\vec{k}\rangle = \frac{\partial\epsilon^n_{\vec{k}}}{\partial(\hbar k_\nu)} \ , \tag{39}$$

rather than the liquid-metal result $\hbar k_\nu/m$. If the Fermi surface is electronlike, we obtain a result for $N_{\mu\nu}$ entirely similar to the liquid-metal case. On the other hand for a holelike Fermi surface, if we assume for simplicity that the band has an ellipsoidal shape, we find $N_{\mu\nu}=-N^h\delta_{\mu\nu}$, where N^h is the number of holes in the band. This is consistent with the common belief that the "hold wind" yields a driving force parallel to the applied field.[21,43,44] However, it implies through the sum rule (36) that we may have treated too simply the polarization response of the "core" electrons. The sum rule in physical terms expresses the fact that, for ohmic conduction, the total force (direct and indirect) on all the nuclei vanishes. Electromigration is a relative motion, even in a pure material. Of course the true direct force on the bare nuclei is always toward the cathode. If in addition we allow the possibility of a hole wind, i.e., an indirect force toward the cathode, then the remainder of the indirect force, which we have presumed throughout this paper may be treated simply as a polarization response leading to an anode directed force, must be of sufficient magnitude to counterbalance in sum both the true direct and the hold-wind indirect forces. To illustrate this restriction imagine that the situation of hole conduction arose from the substitution of N_I impurities into a host, each with bare nuclear charge Z^b-1, one less than that of the host, Z^b. One way that one could then satisfy (36) with the hole-wind result for $N_{\mu\nu}$ would be to presume that the contribution from electron polarization to the indirect force on any nucleus (impurity or host) is Z^beE_μ. Note that this choice is not unique since we only have a sum rule to guide us, but any other choice will lead to the same general conclusion: The total polarization indirect forces outweigh the total direct forces; so if we choose to represent their individual sum on each nucleus as a "direct" force, some of these direct forces would be towards the anode. For the interpretation suggested above, the direct force on a host nucleus would vanish while that on an impurity would be eE_μ; i.e., toward the anode.

Another way of viewing the sum rule is as the requirement that the direct force and wind force must cancel on the average. Hence, in order to predict with confidence the relative direction of electromigration, we need both these forces as a function of atomic configuration. This paper has shown how to calculate the wind force, which arises in the weak net-scattering limit, in such detail. However the treatment of the direct force is probably too crude, especially in crystals. Clearly this point warrants further study so that one can also determine the direct force as a function of atomic configuration and band filling.

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APPENDIX

We show here how to simplify the integral (32). First note that since

$$f_\mu^i = -\frac{\partial}{\partial R_\mu^i} V , \tag{A1}$$

and since T_i is defined by

$$T_i^\pm = V + VG_0^\pm T_i^\pm , \tag{A2}$$

where V is the cluster potential, we may rewrite (32) as

$$\mathcal{V}_{\mu,c}^{-+}(\vec{\mathrm{k}}) = -\langle\vec{\mathrm{k}}|\left(\frac{\partial}{\partial R_\mu^i} T_i^-\right)(1+G_0^- T^-)^{-1}(1+G_0^+ T_i^+)|\vec{\mathrm{k}}\rangle . \tag{A3}$$

Now define

$$\mathcal{G}^\pm = G_0^\pm + G_0^\pm T_i^\pm G_0^\pm = G_0^\pm + G_0^\pm V \mathcal{G}^\pm , \tag{A4}$$

from which one may easily derive

$$\mathcal{G}^\pm V = G_0^\pm T_i^\pm \tag{A5}$$

and

$$\mathcal{G}^+ - \mathcal{G}^- = (1+\mathcal{G}^- V)(G_0^+ - G_0^-)(1+V\mathcal{G}^+) . \tag{A6}$$

Using these we can simplify the factor,

$$(1+G_0^- T_i^-)^{-1}(1+G_0^+ T_i^+) = (1+\mathcal{G}^- V)^{-1}(1+\mathcal{G}^+ V) \tag{A7a}$$

$$= 1+(1+\mathcal{G}^- V)^{-1}(\mathcal{G}^+ - \mathcal{G}^-)V \tag{A7b}$$

$$= 1+(G_0^+ - G_0^-)(1+V\mathcal{G}^+)V \tag{A7c}$$

$$= 1+(G_0^+ - G_0^-)T_i^+ , \tag{A7d}$$

and, hence, write the vertex as

$$\mathcal{V}_{\mu,c}^{-+}(\vec{\mathrm{k}}) = -\frac{\partial}{\partial R_\mu^i}\langle\vec{\mathrm{k}}|T_i^-|\vec{\mathrm{k}}\rangle + 2\pi i \sum_{\vec{\mathrm{l}}}\left(\frac{\partial}{\partial R_\mu^i}\langle\vec{\mathrm{k}}|T_i^-|\vec{\mathrm{l}}\rangle\right)\delta(\epsilon_{\vec{\mathrm{k}}} - \epsilon_{\vec{\mathrm{l}}})\langle\vec{\mathrm{l}}|T_i^+|\vec{\mathrm{k}}\rangle . \tag{A8}$$

The first term will not contribute to (29) because $n_1(\vec{\mathrm{k}})$ is odd in $\vec{\mathrm{k}}$ while $\langle\vec{\mathrm{k}}|T_i^-|\vec{\mathrm{k}}\rangle$ is even in $\vec{\mathrm{k}}$.

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